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Historical perspective on: Transition state theory for collision complexes: Product translational energy distributions [Volume 12, Issue 4, 15 January 1972, Pages 564–568]

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Summary by Dudley Herschbach, Nobel prize-winner: Professor Dudley R. Herschbach.

In the 'early alkali age' of experiments studying reactive collisions in crossed molecular beams, the prototype cases involved abrupt, *impulsive* dynamics, with the products emerging within 10^{-13} s or less. It was expected, however, that suitable systems would form a lingering or *persistent* collision complex with lifetime long compared to rotational as well as vibrational periods. In that regime, the angular and energy distributions of the products would give information about the *unimolecular decomposition* of the complex.

In late 1966, cases that exemplify lingering complexes were, as anticipated, found in exchange reactions of alkali atoms with alkali halides, $A + X^-B^+ \rightarrow A^+X^- + B$. For these reactions, since an ion-pair is present throughout, electron transfer can enhance short-range attraction conducive to forming a statistical collision complex. Direct evidence for persistent complexes appeared in the angular distribution of products, which has symmetry about 90° and peaks very strongly near 0° and 180°. We found the angular distributions could be interpreted in terms of a statistical model akin to the compound nucleus model for nuclear fission. The symmetry indicated that the complex persists for at least several rotational periods, and so has a mean lifetime typically exceeding 5×10^{-12} s. The strong peaking indicated that the typical complex forms and dissociates with centrifugal angular momentum much larger than the rotational momenta of the reactant or product salt molecules. On decomposition of the rotating complex, this centrifugal momentum is converted into relative motion of the emerging product molecules, and hence can significantly affect the exit relative translational energy of the products.

Our 1972 paper in Chemical Physics Letters treated a 'loose complex' defined by the exit and entrance centrifugal barriers associated with long-range attraction. Within the barriers, the energy disposal is assumed to be statistical; outside, the collision partners are assumed to rotate freely and travel like point masses subject to two-body forces. As indicated in Figure 1, we obtained a

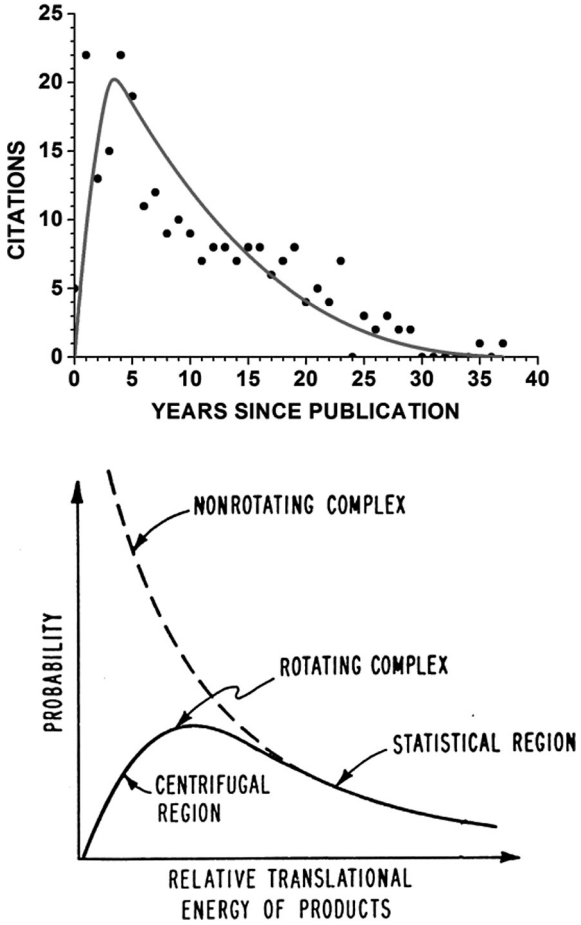

Figure 1. Lower panel: generic form of the product relative translational kinetic energy as predicted from statistical theory, without (dashed curve) and with (full curve) the centrifugal contribution that enters for a rotating complex. Upper panel: distribution of citations over years since publication (calendar year – 1972). Points are from Web of Science; curve corresponds to a four atom (or four author) 'loose complex', with appreciable centrifugal momentum. I thank Dr. Qi Wei for preparing this figure.

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simple, approximate formula for the product relative translational energy, comprised of two factors: statistical and centrifugal. The statistical factor is governed primarily by the densities of rotational and vibrational states at the transition-state, as in the venerable Rice–Ramsberger–Kassel–Marcus (RRKM) treatment of unimolecular reaction rates. That disfavors product translation, since the vibrational and rotational modes are more numerous. The statistical factor thus requires the reaction probability to decline with increase in product translational energy, and the decline becomes more rapid as the number of atoms in the complex increases. In contrast, the centrifugal factor suppresses the product translational energy when it becomes too low to surmount the exit centrifugal barrier.

This simple formula proved to work well for many other persistent complex reactions, beyond the alkali domain. It also encouraged more sophisticated models, applicable to a 'tight' complex. Further discussions are given in Refs. [1–3]. The Web of Science lists 248 subsequent publications citing our 1972 paper in Chemical Physics Letters. Whimsically, I note that the distribution of citations vs. time, shown in the upper panel of Figure 1, resembles the generic product translational energy distribution from a persistent collision complex.

References

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